PALLADIUM - CATALYZED DIMERIZATION OF PROPENE

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Abstract

The insertion of the previously coordinated second molecule of propene into the Pd-C bond is the rate-determining step in the dimerization of propene with the Pd(acac)2 + BF3OEt2 catalyst system. Tetracoordinated square planar Pd hydrides bearing two vacant coordination sites are likely to be catalytically active species in the dimerization of propene. The simplicity of the catalyst system composition might be of industrial importance.

Keywords: Dimerization, palladium, propene

INTRODUCTION

Olefins, particularly ethene, propene, and butenes, are the basic building blocks of the petrochemical industry. They are easily available, cheap, reactive, and readily transferable into a range of useful products. Three types of mechanisms are reported for the dimerization of olefins; (i) degenerated polymerization [1], (ii) concerted coupling [2], and (iii) reductive dimerization [3]. The propene dimers can be regarded as primary products (1-hexene, methyl-1-pentenes and 2,3-dimethyl-1-butene) and products of isomerization.
2-Hexene and 4-methyl-2-pentene could be the products of either isomerization or the primary reaction. Isomerization leads to 3-hexene, 2-methyl-2-pentene (the common isomerization product of 2-methyl-1-pentene and 4-methyl-2-pentene), and 2,3-dimethyl-2-butene.

Palladium β-diketonates and boron trifluoride etherate, BF₃OEt₂, based catalyst systems display high activity and selectivity in the oligomerization, isomerization of alkenes, and telomerization of butadiene with amines [5-7]. This work concerns with some chemical and kinetic aspects of the dimerization of propene with the Pd(acac)₂ + BF₃OEt₂ catalyst system to get more insight into the nature of the catalytically active species.

EXPERIMENTAL

Dimerization of propene was carried out in a thermostated shaking glass reactor with continuous supply of propene. The solution of Pd(acac)₂ in propene atmosphere was kept at desired temperature 10 min and the dimerization was started by the injection of BF₃OEt₂. In standard runs the amount of Pd(acac)₂ was 5x10⁻⁴ M, the total volume was 20 mL, the reaction temperature was 303 K, and toluene was used as a solvent. GLC analyses were made on a “Chrom-42 M” instrument with a copper capillary column L = 100 m, ∅ = 0.35 mm). Squalane was used as a fixed liquid phase.

RESULTS AND DISCUSSION

The interaction of Pd(acac)₂ with BF₃OEt₂ in the presence of 1-hexene involves at the first step the exchange of one acetylacetonate ligand at Pd with BF₃ affording BF₂(acac) and Pd-F moiety. The latter consequently transforms to Pd-F·BF₃ and Pd′BF₄⁻ moieties. The transformation of second chelate acetylacetonate ligand to the monodentate C-bonded mode, and the insertion of 1-hexene into this Pd-C bond and further β-hydride elimination afford the active Pd-H bond at the next step [8]. Pd(acac)₂ with equimolar PR₃ gives the (acac)Pd(C³-acac)PR₃ complex, in which one acetylacetonate ligand is in the monodentate, C-bonded mode. The interaction of this complex with BF₃OEt₂ in the presence of 1-hexene occurs through the protolysis of Pd-C bond to form Pd′BF₄ at the first step. The step of the formation of active Pd-H bond is same to above [9]. The formation of BF₄⁻ anion in these systems was confirmed by the appearance of bands at 529 and 522 cm⁻¹ in IR spectrum of the (acac)Pd(C³-acac)PR₃+2BF₃OEt₂ mixture. The bands were assigned in comparison with IR spectra of a suspension of KBF₄ in mineral oil and of a model reaction of acacH with BF₃OEt₂ to give BF₂(acac) and HBF₄ [9]. Furthermore, Pd(acac)₂ reacts